Mean Fields and Auxiliary Systems

1 Introduction

Mean-field methods replace an interacting many-body problem with a set of independent-particle problems using an effective potential. This effective potential approximates the effects of interactions either in an average sense or as an auxiliary system reproducing selected properties of the interacting system. Such methods are essential in many-body theory as they provide practical starting points for calculations and interpretations of interactions.

Mean-field approximations are crucial in treating interacting, correlated electrons, leading to simplified formulations. When appropriately chosen, these approximations yield physically meaningful results and serve as a foundation for exploring correlation effects. The independent particles in a many-body problem may be the original particles or solutions to mean-field equations optimized to facilitate solving the many-body problem. The key challenge is defining the effective particles correctly.

This lecture focuses on two significant mean-field methods relevant to interacting electron systems: the Hartree-Fock approximation and Density Functional Theory (DFT).

2 Hartree–Fock Approximation

There are two basic independent-particle approaches: the Hartree–Fock approximation to the interacting many-body system and the non-interacting electron methods in which there is a local effective potential. The latter are often referred to as "Hartree-like," after D. R. Hartree who approximated the Coulomb interaction between electrons by an average local mean-field potential. The approaches are similar in that each assumes the electrons are uncorrelated except that they must obey the exclusion principle; however, they are different in spirit and in their interpretation. Hartree-like theories modify the original interacting many-body problem and treat a system of non-interacting electrons in an effective potential. This approach was placed on a firm footing by Kohn and Sham, who showed that one can define an auxiliary system of non-interacting electrons that, in principle, leads to the exact ground-state density and energy.

The Hartree–Fock approximation (HFA) treats directly the system of interacting fermions, with the approximation that the many-body wavefunction is restricted to be an antisymmetrized uncorrelated product function that can be written as a single determinant which explicitly respects the exclusion principle:

$$\Psi_{\mathrm{HF}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1,\sigma_1) & \psi_1(r_2,\sigma_2) & \psi_1(r_3,\sigma_3) & \cdots \\ \psi_2(r_1,\sigma_1) & \psi_2(r_2,\sigma_2) & \psi_2(r_3,\sigma_3) & \cdots \\ \psi_3(r_1,\sigma_1) & \psi_3(r_2,\sigma_2) & \psi_3(r_3,\sigma_3) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} . \tag{1}$$

Here, ψ denotes a single-particle "spin orbital." For our purposes it is sufficient to consider orbitals that are eigenfunctions of $\hat{S}_z$ with spin $\sigma = \pm\frac{1}{2}$ quantized along an axis. Then $\psi_i(r,\sigma)$ is a product of a space orbital $\psi_i^\sigma(r)$ and a spin function. The interaction energy is calculated exactly for this wavefunction so that the resulting total energy is variational, i.e., it is an upper bound to the true ground-state energy E_0. Although the HFA fails qualitatively for metals , and may have large quantitative errors in other cases, it is widely used as the starting point for correlated many-body methods.

The total energy of a system of electrons in an external potential v_{ext} is

$$\langle \Psi_{\text{HF}} | \hat{H} | \Psi_{\text{HF}} \rangle = -\sum_{i,\sigma} \int d\mathbf{r}\, \psi_i^{\sigma *}(\mathbf{r}) \frac{\nabla^2}{2} \psi_i^\sigma(\mathbf{r}) + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n(\mathbf{r}) + E_H + E_x\,. \tag{2}$$

Here, the first term is the kinetic energy of the independent particles,

$$E_H = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}'\, \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\,, \tag{3}$$

is the Hartree contribution (i.e., the classical Coulomb energy), and

$$E_x = -\frac{1}{2} \sum_{\sigma} \sum_{\substack{i,j \\ \text{occ}}} \int d\mathbf{r} \int d\mathbf{r}'\, \psi_j^{\sigma *}(\mathbf{r}')\, \psi_i^\sigma(\mathbf{r}')\, \frac{1}{|\mathbf{r} - \mathbf{r}'|}\, \psi_j^\sigma(\mathbf{r})\, \psi_i^{\sigma *}(\mathbf{r})\,, \tag{4}$$

is the Fock (exchange) term.

Minimization of the total energy with respect to the orthonormal single-particle orbitals ψ_i^σ leads to the Hartree–Fock equations:

$$\begin{aligned} &\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + \sum_{\substack{j,\sigma_j \\ \text{occ}}} \int d\mathbf{r}'\, \psi_j^{\sigma_j *}(\mathbf{r}')\, \psi_j^{\sigma_j}(\mathbf{r}')\, \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right] \psi_i^\sigma(\mathbf{r}) \\ &\qquad - \sum_{\substack{j \\ \text{occ}}} \int d\mathbf{r}'\, \psi_j^{\sigma *}(\mathbf{r}')\, \psi_i^\sigma(\mathbf{r}')\, \frac{1}{|\mathbf{r} - \mathbf{r}'|}\, \psi_j^\sigma(\mathbf{r}) = \varepsilon_i^\sigma\, \psi_i^\sigma(\mathbf{r})\,. \end{aligned} \tag{5}$$

In the first bracket the potential

$$v_H(\mathbf{r}) \equiv \sum_{\substack{j,\sigma_j \\ \text{occ}}} \int d\mathbf{r}'\, \psi_j^{\sigma_j *}(\mathbf{r}')\, \psi_j^{\sigma_j}(\mathbf{r}')\, \frac{1}{|\mathbf{r} - \mathbf{r}'|} = \int d\mathbf{r}'\, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{6}$$

has the Hartree form of a local potential that acts equally on each orbital at point $\mathbf{r}$. It arises from the charge of all the electrons, including a spurious self-interaction that is later canceled by the exchange term. The exchange part involves the non-local Fock operator

$$\hat{x}_\sigma(\mathbf{r}, \mathbf{r}') = -\sum_{\substack{j \\ \text{occ}}} \psi_j^{\sigma *}(\mathbf{r}')\, \frac{1}{|\mathbf{r} - \mathbf{r}'|}\, \psi_j^\sigma(\mathbf{r}) = -\frac{\rho(\mathbf{r}, \sigma;\, \mathbf{r}', \sigma)}{|\mathbf{r} - \mathbf{r}'|}\,, \tag{7}$$

which acts as an integral operator on ψ_i^σ and couples only like spins. Equation (5) represents a coupled set of integro-differential equations that can be solved exactly only in special cases (e.g., spherically symmetric atoms or the homogeneous electron gas). In general, one introduces a basis set so that the equations can be expressed in terms of expansion coefficients and basis function integrals. The HF ground-state wavefunction is the determinant constructed from the N lowest-energy single-particle states.

Excited states can be represented by forming determinants from other combinations of single-particle spin orbitals ψ_i^σ. The eigenvalues of the HF equations 5 correspond to total energy differences (i.e., the energies required to add or remove an electron when all other orbitals are frozen). This is known as Koopmans' theorem. For a fixed number of electrons, excitations (single, double, triple, etc.) can be approximated by replacing ground-state orbitals with empty eigenstates from Eq. (5); the energy difference between the excited state and the ground state then serves as a first approximation to the excitation energy.

In practice, the absence of orbital relaxation in such a scheme often leads to significant overestimations of addition, removal, and excitation energies. In contrast, self-consistent field (SCF) calculations determine energy differences by performing separate self-consistent calculations for the N, $N+1$, or $N-1$ electron systems, allowing all orbitals to relax. For finite systems this approach can yield much more accurate results, while for infinite systems the average relaxation in extended orbitals becomes negligible so that SCF energy differences reproduce the eigenvalues.

In second quantization the origin of the HF "mean field" is particularly transparent. One starts from the full expression for the two-body interaction operator:

$$\hat{V}_{ee} = \frac{1}{2} \sum_{\substack{m,m' \\ n,n'}} \sum_{\sigma,\sigma'} v_{mm'nn'}\, c^\dagger_{m\sigma}\, c^\dagger_{m'\sigma'}\, c_{n'\sigma'}\, c_{n\sigma}\,, \tag{8}$$

where $m, m', n, n' = 1, \ldots, N_{\text{states}}$ refer to the independent-particle basis functions and $v_{mm'nn'}$ denotes the four-center matrix element of the interaction (which may be the bare Coulomb interaction or an effective interaction U). The HFA corresponds to neglecting correlation, so that the four operators in Eq. (8) are factorized into products of single-particle operators:

$$c^\dagger_{m\sigma}\, c^\dagger_{m'\sigma'}\, c_{n'\sigma'}\, c_{n\sigma} \to \Big(< c^\dagger_{m'\sigma'}\, c_{n'\sigma'} > \, c^\dagger_{m\sigma}\, c_{n\sigma} - \delta_{\sigma\,\sigma'} \, < c^\dagger_{m\sigma}\, c_{n'\sigma'} > \, c^\dagger_{m'\sigma'}\, c_{n\sigma} \Big). \tag{9}$$

In this factorization the first term gives rise to the Hartree potential (involving the density operator), and the second term produces the exchange term that couples only like spins. Note that for the case $n' = n$, $m' = m$, and $\sigma = \sigma'$ the unphysical self-interaction cancels exactly.

In a plane-wave basis the Coulomb matrix elements are determined by the Fourier components

$$v_c(q) = \frac{4\pi}{q^2}\,.$$

Then the interaction can be expressed as

$$\hat{V}_{ee} = \frac{1}{2} \sum_{q} \sum_{\substack{k,\sigma \\ k',\sigma'}} v_c(q)\, c^\dagger_{k+q,\sigma}\, c^\dagger_{k'-q,\sigma'}\, c_{k'\sigma'}\, c_{k\sigma}\,, \tag{10}$$

where q is the momentum transfer in the interaction.

For a lattice model the interaction is often most conveniently written in terms of site operators. For example, in the one-band Hubbard model the Hartree–Fock approximation can be written as a sum over sites i,

$$U\sum_i \hat{n}_{i\uparrow}\,\hat{n}_{i\downarrow} \to U\sum_i \Big[\langle\hat{n}_{i\uparrow}\rangle\,\hat{n}_{i\downarrow} + \hat{n}_{i\uparrow}\,\langle\hat{n}_{i\downarrow}\rangle\Big], \tag{11}$$

where U is the on-site interaction and $\hat{n}_{i\sigma} = c^\dagger_{i\sigma}\,c_{i\sigma}$.

3 Density Functional Theory and the Kohn–Sham Auxiliary System

Density functional theory (DFT) is a theory of the interacting many-electron system.[1] In this course we focus on aspects of DFT that are motivated by its conceptual relation to later methods (e.g., Green's functions and quantum Monte Carlo) and by its practical role as a starting point for many-body calculations. The theory inherently reflects the many-body nature of the problem—for example, DFT is pursued up to the strong-interaction limit where electrons form a Wigner crystal. DFT is included in this "mean-field" chapter because the Kohn–Sham (KS) construction of an auxiliary system provides a framework in which the solution can be obtained using mean-field methods. Its detailed review here is justified by its importance for quantitative many-body calculations and for subsequent developments in the field.

3.1 Preliminaries

Density functional theory (DFT) provides the theoretical framework within which most of the modern first-principles simulations of condensed matter and molecular physics are performed. It has proven to be extremely successful, and is the basis of numerous first-principles simulations in solids, liquids, atoms, and molecules, covering a variety of contexts—from planetary sciences to biosciences and engineering (including, of course, solids and materials).

We will see here the fundamentals of the theory, which is a ground state theory. (It was generalized to equilibrium at finite temperatures and to dynamical, i.e., non-equilibrium, situations; however, we will focus here on the original ground state theory.) The theory rests on two important landmark papers. In the first one (P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964) it was shown that when solving for the ground state, the quantum mechanical variational principle for

$$\langle\Psi|\hat{H}|\Psi\rangle,$$

and, consequently, the ground state energy expressed as a functional of Ψ, can be replaced by a variational principle for the energy as a functional of the particle density,

$$E\big[\Psi(\{s_i\})\big] \quad\longrightarrow\quad E\big[n(\mathbf{r})\big]\,. \tag{12}$$

This represents an enormous gain: instead of working with a function defined in a $3N$-dimensional space, we only need to handle a function in 3-dimensional space!

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[1] Density functional theory for classical liquids was developed before the work of Hohenberg and Kohn. Perhaps the first density functional theory was introduced by van der Waals in 1894 to describe capillary action in liquids. This approach was later revived by Cahn and Hilliard in 1958.

The second paper (W. Kohn and L. J. Sham, *Phys. Rev.*, 1965) proposed a practical way to use the former concept. It transformed the original problem into a mean-field-like problem of non-interacting electrons moving in a suitably defined effective potential, as illustrated in the figure below.

The theoretical framework does not imply approximations; it is exact for the electronic subsystem within non-relativistic quantum mechanics. Practical calculations, however, will be approximate.

We continue by assuming the adiabatic decoupling of nuclear and electron dynamics following the Born–Oppenheimer approximation described earlier. That is, we solve the electronic problem for nuclear positions fixed in space (and therefore as a function of nuclear positions). These nuclei give rise to an external potential acting on the electrons. Whether the system is a piece of DNA or a piece of metal, different systems will be associated with a different external potential for the electrons.

3.2 The Hohenberg-Kohn Formulation and the Levy-Lieb constrained search

The total energy of an interacting many-electron system may be written as a sum of the electron-only terms plus the effect[2] of the external potential $v_{\text{ext}}(\mathbf{r})$ due to the nuclei and other sources:

$$E = \langle \hat{H} \rangle = \langle \hat{T} + \hat{V}_{ee} \rangle + \int d\mathbf{r}\; v_{\text{ext}}(\mathbf{r})\, n(\mathbf{r})\,. \tag{13}$$

This expression is defined for a range of many-body wavefunctions and densities $n(\mathbf{r})$. Minimizing over all normalized, antisymmetric wavefunctions yields the ground state with density n_0 and total energy E_0. Since E_0 is determined by the external potential $v_{\text{ext}}(\mathbf{r})$, each term in Eq. (13) for $\Psi = \Psi_0$ is, in effect, a functional of v_{ext} (often denoted with square brackets as in $E[v_{\text{ext}}]$). Notice that the quantum system's state at any point $\mathbf{r}$ depends on the potential everywhere.

Hohenberg and Kohn showed that the energy can also be expressed as a functional of the density:

$$E_{\text{HK}}[n] = F_{\text{HK}}[n] + \int d\mathbf{r}\; v_{\text{ext}}(\mathbf{r})\, n(\mathbf{r})\,, \tag{14}$$

where

$$F_{\text{HK}}[n] = \langle \hat{T} \rangle + \langle \hat{V}_{ee} \rangle$$

is universal (i.e., the same for all electron systems). This result, which is an example of a Legendre transformation , implies a one-to-one relation between n and v_{ext} (for densities that are *v-representable*). The ground state is found by minimizing $E_{\text{HK}}[n]$ over all such densities.

The issue of v-representability is circumvented by the two-step constrained search formulation introduced by Levy and Lieb. In this approach, one first defines a functional for a given density $n(\mathbf{r})$ by minimizing the expectation value of $\hat{T} + \hat{V}_{ee}$ over all wavefunctions Ψ that yield $n(\mathbf{r})$:

$$E_{\text{LL}}[n] = \min_{\Psi \to n} \langle \hat{T} + \hat{V}_{ee} \rangle + \int d\mathbf{r}\; v_{\text{ext}}(\mathbf{r})\, n(\mathbf{r})\,. \tag{15}$$

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[2] It is assumed here that no magnetic field is present. (Zeeman terms can be added in spin-density functional theory to describe magnetic systems

(Any many-body wavefunctions yielding the same density are acceptable; for instance, any plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ produces a uniform density.) The second step is then to minimize $E_{\mathrm{LL}}[n]$ with respect to $n(\mathbf{r})$. Both the HK and LL formulations lead to the same ground state at the energy minimum.

3.3 Preliminary Exercises

In what follows we will use two formal results which are easy to prove (see appendix to this chapter notes). Firstly, it is straightforward to show that for a set of indistinguishable independent particles the particle density is given by

$$n(\mathbf{r}) = \sum_{\mathrm{occ}\ i} \left|\psi_i(\mathbf{r})\right|^2 . \tag{16}$$

This expression generalizes to electrons with spin as follows:

$$n(\mathbf{r}) = \sum_{\mathrm{occ}\ i,\sigma} \left|\psi_{i\sigma}(\mathbf{r})\right|^2 = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}) \, , \tag{11.3}$$

$$n_\sigma(\mathbf{r}) = \sum_{\mathrm{occ}\ i} \left|\psi_{i\sigma}(\mathbf{r})\right|^2 , \tag{11.4}$$

and the spin density is defined as

$$n_s(\mathbf{r}) = n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r}) \, . \tag{17}$$

Secondly, consider a general many-particle wave-function $\Psi(\{s_i\})$, and a local potential energy operator (which is multiplicative in the local representation) of the form

$$\hat{V} = \sum_{i=1}^{N} V_{\mathrm{ext}}(\mathbf{r}_i) \, , \tag{18}$$

where $V_{\mathrm{ext}}(\mathbf{r})$ is a function of position in 3D and N is the number of particles. One can prove that

$$\langle \Psi | \hat{V} | \Psi \rangle = \int d^3 r \, n(\mathbf{r}) \, V_{\mathrm{ext}}(\mathbf{r}) \, . \tag{19}$$

3.4 The Hohenberg–Kohn Theorems

We do not follow the original Hohenberg–Kohn paper rather, we adopt the formulation of Levy (see M. Levy, Proc. Natl. Acad. Sci. 76, 6062 (1979)) as described in the review by Jones and Gunnarsson [Rev. Mod. Phys. 61 692 (1989)]. Let us write the very general many-electron Hamiltonian as

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ee} \, , \tag{20}$$

with

$$\hat{T} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 \, , \tag{21}$$

$$\hat{V} = \sum_{i=1}^{N} V_{\mathrm{ext}}(\mathbf{r}_i) \, , \tag{22}$$

$$\hat{V}_{ee} = \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \, . \tag{23}$$

For a non-degenerate ground state, we now state the following two results:

- **Theorem I:** For a many-fermion system under the influence of an external local potential
$$\hat{V} = \sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i),$$
an energy functional of the particle density can be defined as
$$E\big[n(\mathbf{r})\big] = F\big[n(\mathbf{r})\big] + \int d^3r \, n(\mathbf{r}) \, V_{\text{ext}}(\mathbf{r}) \, , \tag{24}$$
where $F[n(\mathbf{r})]$ is a universal functional of the density, and
$$E\big[n(\mathbf{r})\big] \geq E_{\text{GS}} \, . \tag{25}$$
- **Theorem II:**The inequality in the eq. above becomes an equality only when the density is that of the ground state, i.e.,
$$E\big[n_{\text{GS}}(\mathbf{r})\big] = E_{\text{GS}} \, . \tag{26}$$

These statements represent a variational principle equivalent to that of conventional quantum mechanics, but with the enormous advantage that one only needs to vary and optimize a function of three variables instead of a function defined in $3N$ dimensions.

3.5 On Density representability and locality

3.5.1 v-Representability in the Hohenberg–Kohn Theorems

In Density Functional Theory (DFT), one of the central ideas is that the ground-state properties of an interacting many-electron system can be uniquely determined by its electron density $n(\mathbf{r})$. The original Hohenberg–Kohn (HK) theorems establish a one-to-one correspondence between the ground-state density and the external potential $v_{\text{ext}}(\mathbf{r})$ (up to an additive constant). However, a key assumption in their proofs is that the densities under consideration are *v-representable.*

A density $n(\mathbf{r})$ is said to be *v-representable* if there exists some local external potential $v_{\text{ext}}(\mathbf{r})$ for which $n(\mathbf{r})$ is the ground-state density of the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i) \, .$$

That is, $n(\mathbf{r})$ is v-representable if it can be obtained as the solution (i.e., the ground-state density) of the Schrödinger equation for some local potential $v_{\text{ext}}(\mathbf{r})$.

3.5.2 What Does It Mean for a Potential to be *Local*?

A potential is said to be *local* if it acts multiplicatively in the position (coordinate) representation. This means that, when expressed in the coordinate basis, the potential operator does not mix different positions; instead, it acts directly by multiplication by a function of position.

For example, consider a one-particle potential $v(\mathbf{r})$. In the coordinate representation, its action on a wave function $\psi(\mathbf{r})$ is given by:

$$[\hat{v}\psi](\mathbf{r}) = v(\mathbf{r})\,\psi(\mathbf{r}).$$

Notice that the operator $\hat{v}$ is diagonal in the coordinate basis.

In the context of many-body systems, if the potential energy operator for N particles can be written as

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i),$$

then each term $v(\mathbf{r}_i)$ depends only on the position of the ith particle. When this operator acts on a many-body wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, we have:

$$[\hat{V}\Psi](\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^{N} v(\mathbf{r}_i)\,\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N).$$

This separability into a sum of one-particle potentials is what is meant by the potential being *local*.

In contrast, a *non-local* potential does not act solely by multiplication at a single point. Instead, it may involve an integral operator that couples the wave function at different points. For instance, a non-local potential might be written as:

$$[\hat{V}\psi](\mathbf{r}) = \int d\mathbf{r}'\,V(\mathbf{r}, \mathbf{r}')\,\psi(\mathbf{r}'),$$

where the value at $\mathbf{r}$ depends on $\psi(\mathbf{r}')$ for other values of $\mathbf{r}'$.

3.5.3 Importance in the Hohenberg–Kohn Theorems

The v-representability condition is crucial in the original HK proofs for two main reasons:

- **One-to-One Mapping:** The HK theorems rely on the assumption that the density $n(\mathbf{r})$ comes from some local potential. Under this assumption, they prove that if two different external potentials yield the same ground-state density, then the potentials can differ only by an additive constant. This one-to-one correspondence between $v_{\text{ext}}(\mathbf{r})$ and $n(\mathbf{r})$ is fundamental to formulating DFT.

- **Variational Principle:** The ground-state energy is expressed as a functional of the density,

$$E[n] = F[n] + \int d\mathbf{r}\,v_{\text{ext}}(\mathbf{r})\,n(\mathbf{r})\,,$$

  and the proof that the minimum of $E[n]$ equals the true ground-state energy E_{GS} relies on restricting the domain of $n(\mathbf{r})$ to those densities that are v-representable.

3.5.4 Limitations and Later Developments

Not every mathematically acceptable density (i.e., any nonnegative function that integrates to the correct number of electrons) is v-representable. There may exist densities that cannot be obtained as the ground-state density for any local potential. Consequently, the original HK proofs apply only to the subset of densities that are v-representable.

Later developments, such as the constrained search formulation by Levy and Lieb, relax this restriction by considering the broader concept of *N-representability*—requiring only that the density originates from some antisymmetric N-electron wavefunction, regardless of whether it is produced by a local potential. This generalization makes the theory more practical and applicable to a wider range of systems.

3.6 The Levy Construction

Levy proposed the following functional for an *N-representable* particle density $n(\mathbf{r})$ (i.e., one that can be obtained from an antisymmetric N-electron wave-function):

$$F\big[n(\mathbf{r})\big] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \,, \tag{27}$$

where the minimization is performed over all N-particle wave-functions Ψ that yield the density $n(\mathbf{r})$. This concise expression means that $F[n(\mathbf{r})]$ is given by the minimum possible expectation value of $\hat{T} + \hat{V}_{ee}$ among all N-particle wave-functions that produce the specified density $n(\mathbf{r})$. Although we have just written a concise definition for $F[n(\mathbf{r})]$, its practical evaluation is much more complex than solving the full quantum problem; hence, it is used mainly to establish the theoretical framework.

3.7 Proof of First Theorem

Let us rewrite Eq. (27) in a more compact form:

$$F\big[n(\mathbf{r})\big] = \langle \Psi_n^{\min} | \hat{T} + \hat{V}_{ee} | \Psi_n^{\min} \rangle \,. \tag{28}$$

Then, by adding the contribution from the external potential, we have

$$F\big[n(\mathbf{r})\big] + \int d^3r \, n(\mathbf{r}) \, V_{\text{ext}}(\mathbf{r}) = \langle \Psi_n^{\min} | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi_n^{\min} \rangle \geq E_{\text{GS}} \,, \tag{29}$$

which is a direct consequence of the quantum mechanical variational principle (since the right-hand side is the expectation value of the Hamiltonian for some trial many-electron wave-function).

3.8 Proof of Second Theorem

To prove that

$$E\big[n_{\text{GS}}(\mathbf{r})\big] = E_{\text{GS}} \,, \tag{30}$$

we start with the variational principle applied to the ground state:

$$E_{\text{GS}} = \langle \Psi_{\text{GS}} | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi_{\text{GS}} \rangle \leq \langle \Psi_{n_{\text{GS}}}^{\min} | \hat{T} + \hat{V}_{ee} + \hat{V} | \Psi_{n_{\text{GS}}}^{\min} \rangle \,. \tag{31}$$

Since the external potential operator $\hat{V}$ depends only on the density, its expectation value is the same for both wave-functions. Removing it from both sides, we obtain

$$\langle \Psi_{\rm GS} | \hat{T} + \hat{V}_{ee} | \Psi_{\rm GS} \rangle \leq \langle \Psi^{\rm min}_{n_{\rm GS}} | \hat{T} + \hat{V}_{ee} | \Psi^{\rm min}_{n_{\rm GS}} \rangle \,. \tag{32}$$

By the very definition of $\Psi^{\rm min}_{n_{\rm GS}}$, the reverse inequality must also hold; hence, we conclude that

$$\langle \Psi_{\rm GS} | \hat{T} + \hat{V}_{ee} | \Psi_{\rm GS} \rangle = \langle \Psi^{\rm min}_{n_{\rm GS}} | \hat{T} + \hat{V}_{ee} | \Psi^{\rm min}_{n_{\rm GS}} \rangle \,. \tag{33}$$

It then follows that

$$E_{\rm GS} = \langle \Psi_{\rm GS} | \hat{T} + \hat{V}_{ee} | \Psi_{\rm GS} \rangle + \int d^3r \, n_{\rm GS}(\mathbf{r}) \, V_{\rm ext}(\mathbf{r}) = \langle \Psi^{\rm min}_{n_{\rm GS}} | \hat{T} + \hat{V}_{ee} | \Psi^{\rm min}_{n_{\rm GS}} \rangle + \int d^3r \, n_{\rm GS}(\mathbf{r}) \, V_{\rm ext}(\mathbf{r}) \,, \tag{34}$$

or, equivalently,

$$E\big[n_{\rm GS}(\mathbf{r})\big] = F\big[n_{\rm GS}(\mathbf{r})\big] + \int d^3r \, n_{\rm GS}(\mathbf{r}) \, V_{\rm ext}(\mathbf{r}) = E_{\rm GS} \,.$$

3.8.1 Conclusion

This Lecture has provided the formal framework for density functional theory in terms of a variational principle on a functional that is known to exist, even though its explicit form is unknown. The theory as presented is exact for the ground state of any many-particle system, regardless of the degree of electron correlation.

For practical calculations, however, one must introduce approximations to the universal functional $F[n(\mathbf{r})]$. One line of research—called orbital-free density functional theory—aims to develop approximate functionals for both the kinetic energy and the electron–electron repulsion energy. Although these methods are computationally extremely efficient (since one deals only with a function in three dimensions), they have not yet achieved the systematic accuracy needed for widespread use.

The contribution of Walter Kohn and Lu J. Sham (published one year after the work of Hohenberg and Kohn) gave rise to the way DFT calculations are performed today. In the next Lecture we will build on these ideas.